Methodology and sample holder for analyses under quarantine of Martian Return Samples,

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Introduction: In the last few years, starting with the NASA Stardust mission, the analysis of return samples has been revived and upgraded. The obvious goal is to multiply this type of analyses and the years to come will see the advent of other return sample missions such as the Japanese Hayabusa mission, the Russian Phobos Grunt mission and the NASA Mars Return Sample mission. All these projects have been designed in the perspective of a direct sample return, following the older sample return missions by the Apollo 11 and 12 landers, the Russian Luna ones and the last in line, the NASA Genesis one.

It is generally agreed that the upcoming sample return missions may be returning samples containing potential biohazards such as microorganisms which may have withstood the rigors of space travel. Analysis of these samples can be performed in a facility equipped for the planetary protection conditions of biosafety level 4 (BSL4), guaranteeing no contamination of the Earth by these samples as well as the reverse situation. Alternatively, for analyses in terrestrial large facility laboratories such as synchrotrons and particle accelerators these samples can be sterilized and released for direct manipulation. Our goal is to actually offer an alternative possibility of analyzing these samples in facilities at large, using optimized experimental setups while keeping the samples in conditions of quarantine. Our design allows *in-situ* analysis of extraterrestrial grains and offers the advantage of avoiding sample alteration which necessarily follows current sterilization procedures of high temperature > 125°C bake-out or gamma rays bombardment. Our methodology is derived from the analyses of meteorites [1-3] and cometary and/or interstellar grains from the recent NASA Stardust mission [4-7]. These samples have been analyzed using a succession of synchrotron radiation (SR) nondestructive probes fielded at the ID22 beamline dedicated to micro-fluorescence/tomography/diffraction on the ESRF synchrotron in Grenoble, France. The same SR analysis protocols as well as several other lab-based ones are proposed for the upcoming return samples. The methodology we propose has been optimized during numerous experiments in the course of the last 10 years and it allows a qualitative and absolute quantitative analysis in nondestructive and noninvasive conditions.

SR protocol: For grains of several hundred microns diameters, an X-ray beam of 1 x 1 μm^2 will be used. The monochromatic SR microbeam of 10 - 30 keV will be delivered by a high throughput double mirror K-B focusing device. The first probe to be applied to the Martian grains is the X-ray fluorescence spectroscopy, at the appropriate spatial resolution, congruent with the grain size. The fluorescence output is primarily qualitative and can be obtained by scanning the sample in front of the beam. All elements from Z=14 (Si) to Z=92 (U) can be thus imaged in the grain. The absolute quantification is much more difficult as the grain has a size which exhibits strong self-absorption for the X-rays emitted in the bulk. However, an accurate quantitative analysis can be performed on the grains by means of fluorescence tomography, a technique combining fluorescence spectroscopy and 3D tomography scanning [8, 9]. While performing the first 2D map of the grains, simultaneous with the fluorescence analysis, micro-diffraction of powder samples is performed and recorded on a CCD camera located behind the sample-holder. A 2D image of the grains can thus be obtained if polycristalline micro-phases are present. Once an approximated map of the grains has been obtained, we can perform a micro-speciation analysis in order to record Xanes spectra at K edges of selected elements, such as S, Ca, Fe, Zn. The Xanes analysis will be performed in fluorescence mode at hotspots preliminary identified by the fluorescence qualitative mapping. Absorption micro-tomography can then be performed in full-beam mode to record the 3D morphology of the grain. If necessary, a lengthier fluorescence-tomography scan can then be performed using the focused beam mode, in order to obtain a 3D elemental image of the grain.

Lab-based protocol: These measurements are performed on standard laboratory microscopes of two kinds: Raman and IR. Raman spectroscopy can be performed down to a 1 μm^2 resolution, in order to directly obtain the mineralogy of the surface layer of the grain.

As Raman penetration capability is of only a few tens of nm, only the grain outer layer will be imaged but that will give much-needed information to validate the elemental results obtained from the X-ray fluorescence. Direct mineralogical analysis will be possible for silicate or carbonate grains or some oxides/sulfides easily identified by Raman spectroscopy. The IR microscopy, performed in the FT-IR mode will allow the identification of organic phases or at the very least carbon phases or hydrated minerals.

Sample-holder: A miniaturized sample-holder has been designed for allowing direct analysis of a collection of extraterrestrial grains confined in a triple container and positioned remotely in front of the X-ray or laser beams of the various setups. The grains are held by several silica capillaries featuring very thin walls (10 µm) which are both sufficiently resistant to allow straightforward grain manual/remote-controlled micromanipulation but sufficiently thin to be semitransparent for the emitted X-rays, Raman and IR beams. Optimized windows have been designed for all analyses and fitted to the three walls of confinement. They are made of thin Be with reduced absorption for the X-rays and transparent sapphire for the laser ones. The whole sample-holder is designed to allow installation on a synchrotron beamline drive or in a laboratory based microscope. It is miniaturized and made of light but sturdy materials allowing easy monitoring of the pressure and temperature by embarked microsensors, thus allowing an accurate diagnostic of the containment of the grain set. Microsensors of pressure and temperature are mounted in each of the three confinement chambers and interrogated by a PC-based acquisition software. The sample holder insures both BSL4 planetary protection conditions of analysis as well as sample non-contamination by terrestrial microorganisms.

Quantitative data treatment: In order to obtain accurate quantitative results for the projected combined measurements in the sample holder, a Monte-Carlo X-ray fluorescence simulation code[8] was extensively used. This code models monochromatic, polarized photon interacting with homogeneous samples and includes fluorescence as well as Compton and Rayleigh scattering. The code can be used in a feedback loop to generate absolute quantitative concentrations of elements in homogeneous samples in order to match reference materials. An X-ray database[9] providing fluorescence, coherent and incoherent scattering cross sections was used to obtain elemental absolute masses. The ESRF PyMCA[10] hyperspectral data analysis code is used to fit X-ray lines and to perform multi-dimensional imaging using the fluorescence, diffraction, Raman and IR spectroscopy signals.

We will present details of our measurement protocol and of the sample-holder design as well as benchmark results of analyses of standard grains of minerals obtained from some of the probes mentioned, in order to qualify our methodology and prototype.

References:

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